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(54) Title: LOW OXYGEN TRANSMISSIVE FILM

(57) Abstract

A low oxygen transmissive film combination having a substrate with a surface having a surface free energy of at least about 35 dynes/cm, a primer coating on one or both sides and an oxygen transmissive inhibiting layer of a poly(vinyl alcohol) and a cross-linking agent with a proportion of catalytically active sulfuric acid.

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LOW OXYGEN TRANSMISSIVE FILM

This invention relates to a flexible, multilayer film having low oxygen transmissive characteristics.

Certain polymeric films employed for the packaging of foods inherently permit the transmission of oxygen from the outside of the film to the inside of a package made up of the film. Oxygen permits rapid deterioration of foods packaged in such a container, therefore, its exclusion or control is desired.

In accordance with the present invention, a film combination comprises a polymeric substrate susceptible of transmitting oxygen, at least one side thereof having been treated to a surface-free energy of at least 35 dynes/cm; at least one treated side having a primer coating thereon; and on the primer coating, an oxygen transmission inhibiting layer of poly(vinyl alcohol) containing a cross-linking agent catalyzed with sulfuric acid.

The substrates contemplated herein include any polymeric film substrate oriented or unoriented which inherently permits the transmission of oxygen and wherein the utility of such film would call for a minimization of the transmission of oxygen. In most cases, the source of the oxygen referred to herein is atmospheric oxygen. While nylon, polyethylene terephthalate and polycarbonate, films are contemplated herein, a particularly preferred class of films are the polyolefins. Within the polyolefin class, homopolymers and copolymers of propylene are preferred.

Particularly preferred are isotactic polypropylenes containing at least 80% by weight of isotactic polypropylene. The preferred base substrate layer can be homopolypropylene having a melting point range from 321° to 336°F. A commercially available material of this description is ARCO W472. The preferred substrate can also be coextruded with a thin

skin layer, in an amount from 2 to 12% of the total thickness, of a copolymer of propylene and another olefin, e.g., ethylene and/or butene-1. The other olefin can be present in the copolymer in an amount from 1 to 7 wt%.

In order to inhibit effectively the amount of oxygen transmitted through the base layer, the base layer must be 1) treated to a surface free energy of at least 35 dynes/cm, 2) have a primer coating applied thereto, and 3) have a coating on the primer of an oxygen transmission inhibiting layer of poly(vinyl alcohol) containing a cross-linking agent catalyzed with sulfuric acid.

The preferred substrate must be properly prepared to receive the primer layer followed by the cross-linked poly(vinyl alcohol). This proper treatment involves treating the surface to a surface tension level of at least 35 and preferably from 38 to 45 dynes/cm in accordance with ASTM Standard D2578-84. The treatment can be flame treatment, plasma treatment, chemical treatment or corona discharge treatment. Flame treatment and corona discharge treatment are preferred with corona discharge treatment being particularly preferred.

Commercially available corona discharge treatment equipment can be obtained from Solo Systems, Inc., Garland, Texas; Corotec Corporation, Collinsville, Connecticut; Softal Electronics, Hamburg, W. Germany; and others. Using, for example, Softal Electronics equipment, a treater can have an air gap of about 0.050 in. when treating polypropylene film of about 0.9 mils. The film can be treated to a surface free energy from 42 to 44 dynes/cm.

After this treatment, a suitable primer material is coated onto the treated surface.

Preferred primer materials are those disclosed in U.S. Patent No. 4,564,559. These include a primer produced by condensing a monoaldehyde with an interpolymer of acrylamide or methacrylamide and at least one other unsaturated monomer. Further included is a material resulting from condensing aminoaldehyde with acrylamide or methacrylamide and subsequently interpolymerizing the condensation product with at least one other unsaturated monomer in the presence of a C_1-C_6 alkanol. A preferred primer coating resin of this type comprises a copolymer containing up to 90% by weight of styrene, up to 80% by weight of an alkyl acrylate, up to 15% by weight of methacrylic acid and 5% to 25% by weight of acrylamide which has been condensed with a solution of formaldehyde in n-butanol containing from 0.2 to 3 equivalents of formaldehyde for each amide group in the copolymer. Another primer resin of this type is a 50% solid solution of a copolymer resin containing 38.5 parts of styrene, 44 parts of ethyl acrylate, 2.5 parts of methacrylic acid and 15 parts of acrylamide which has been condensed with 5.2 parts of formaldehyde in n-butanol.

A particularly preferred primer material for the structure contemplated herein has been found to be poly(ethyleneimine). The imine primer provides an overall adhesively active surface for thorough and secure bonding with the subsequently applied cross-linked poly(vinyl alcohol). It has been found that an effective coating solution concentration of the poly(ethyleneimine) applied from either aqueous or organic solvent media, such as ethanol, is a solution comprising from 0.1 to 0.6% by weight of the poly(ethyleneimine). A commercially available material of this type is known as Polymin P, a product of BASF-Wyandotte Corporation.

Another particularly preferred primer material is the reaction product of an epoxy resin with an acidified aminoethylated vinyl polymer. The contemplated epoxy resins are glycidyl ethers of polyhydroxy compounds. Typical polyhydroxy compounds which may be used include bisphenol A, ring-substituted bisphenol A, resorcinol, hydroquinone, phenol-formaldehyde, Novolac resins, aliphatic diols, such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexane-diol, glycerol, lower alkyl hydantoins and mixtures thereof. The preferred epoxy resins of the present invention are those made by the glycidation reaction between epichlorohydrin and bisphenol A. Epoxy resins of this type are commonly classified by their epoxy equivalent weight (EEW) which is defined by the weight of resin in grams which contains one gram equivalent of epoxy groups. Resins with an EEW from 170 to 280 may be used in the present invention, but the preferred range is 180 to 210.

Although the specific structure of the epoxy resin is not critical to the primer employed in the present invention, important considerations in the selection of the epoxy resin revolve around its physical state. For example, it must be liquid and capable of being readily dispersed or dissolved with the second component or curing agent as described hereinbelow. If the epoxy resin is of low viscosity, it may be stirred directly into the second component, i.e., curing agent, however, it is preferred to employ the epoxy resin in an aqueous emulsion.

The second component in the epoxy primer composition of the present invention is an amino modified acrylic polymer which is water soluble. This polymer is a curing agent for the epoxy compound. The preferred material is described in U.S. Patent No.

3,719,629. This material may be generically described as an acidified aminoethylated interpolymer having pendent aminoalkylate groups. This material is produced by polymerizing acrylate, methacrylate, styrene or other suitable monomers with sufficient methacrylic or acrylic acids to give a -COOH content of 7.5 to 12.5%. Solvent polymerization techniques are preferred. The polymer is then reacted with ethyleneimine monomer and acidified with hydrochloric acid to render the polymer water-soluble.

In one embodiment of the present invention, a liquid epoxy resin is emulsified in a solution of the curing agent by rapid stirring, the resultant dispersion is diluted with water to the desired concentration for coating, usually from 2 to 20% solids. When mixing the epoxy resin with the curing agent, it is generally preferred to use a stochiometric equivalent balance of epoxy and amine groups.

However, it has been found that the stochiometric ratio may be varied over a wide range, from 1 epoxy to 3 amine groups through 3 epoxy groups to 1 amine group. Any of the above described primers can be employed in an amount from 0.001 to 3.5 g/m^2.

The poly(vinyl alcohol) employed herein can be any commercially available material. For example, ELVANOL 71-30, an E. I. duPont product. The poly(vinyl alcohol) coating solution is prepared by dissolving the polymer in hot water, cooling and mixing both with a suitable cross-linking agent and sulfuric acid as the catalyst. The cross-linking agent can be a melamine- or urea-formaldehyde resin. Commercially available cross-linkers also would include PAREZ 613, a methylated melamine formaldehyde; CYMEL 373, a methylated melamine formaldehyde; CYMEL 401, a trimethylol melamine urea formaldehyde; glyoxal, borax,

etc. Sulfuric acid as the cross-linker catalyst has been discovered to be far superior to nitric acid, ammonium chloride and ammonium nitrate.

Cross-linking is carried out to make the poly(vinyl alcohol) less moisture sensitive but it is essential that this does not occur before the coating weight is applied and evenly distributed. This is effected by making up the aqueous solution so that the initial concentration is too low for this to occur but, as drying occurs, the concentration increases and the rate of cross-linking is heightened.

Suitable concentrations have been found to be from 1 to 35, preferably from 4 to 8 wt% of the solution, being polymer plus cross-linking agent plus sulfuric acid in a catalytically active amount. If the solids content is higher, the solution becomes too viscous; if lower, good water resistance is not obtained. From 5% to 30%, typically 15% cross-linking agent is used with from 0.1% to 7.5%, typically 2% of the sulfuric acid catalyst. A preferred formulation comprises the following solids content: 85.5 wt% poly(vinyl alcohol); 12.8 wt% methylated melamine formaldehyde; and 1.7 wt% sulfuric acid. The sulfuric acid employed can have a strength from 0.1 to 1.0, molarity. A catalytically active amount can be from 0.1 to 20 wt. %.

The aqueous poly(vinyl alcohol) solutions were prepared by dissolving sufficient ELVANOL 71-30 in hot water to form 8 wt% solutions which were then cooled. To these solutions were added a 20 wt% aqueous melamine formaldehyde solution and the appropriate amount of aqueous ammonium chloride solutions and sulfuric acid solutions to provide the formulations shown in the Table below. The cross-linked poly(vinyl alcohol) can be present in from 0.2 to 3 g/m^2.

Examples

Samples as shown in the following Table were prepared as follows: A homopolymer polypropylene core is coextruded with skin layers of an ethylene-propylene random copolymer. The random copolymer contains approximately 3-5% by weight of ethylene. The extruded film is biaxially oriented to 4-5 times machine direction and 7-10 times transverse direction to yield a film having a thickness of approximately 1 mil. The thickness of the skin layers is approximately 12% of the film and are approximately of equal thickness. This film combination is corona discharge treated in accordance with commonly employed prior art techniques to produce a surface with a wetting tension of about 42 dynes/cm. The treated film is precoated on both sides with 0.1 wt% poly(ethyleneimine), i.e., the above-identified BASF-Wyandotte Corporation Polymin P product. The film is air-dried at 100°C. This coating weight is too low to be measured, but is calculated to be in the range of 0.002 grams per m^2. This primer coated treated substrate is then coated on one side with an acrylate coating to a coating weight of about 1.0 g/m^2. If PVOH is applied first, the barrier is improved. This is due to the additional heat that is used to dry the acrylic. This acrylate coating is an aqueous ammoniacal solution of terpolymer latex resulting from the polymerization of about 56% by weight of methyl methacrylate, about 40% by weight of methyl acrylate, and about 4% by weight of methacrylic acid. The opposite surface of this film structures was coated with the appropriate solution of poly(vinyl alcohol), cross-linking agent and catalyst. The solutions were applied utilizing a reverse direct gravure coater and the coated film is passed through a

dry-air oven at from 100-125°C. This produces a coating weight of 0.5 g/m^2.

The dried films are then tested in an oxygen-permeability device in which a stream of dry oxygen is passed through an aqueous salt solution-permeated pad to control the gas moisture content and then through the films, disposed at right angles to the stream, with the cross-linked poly(vinyl alcohol) coating upstream. The oxygen transmitted was determined and the amount of oxygen passed per unit area of film per time period is calculated. The sulfuric acid catalyzed systems are superior to any other catalyzed system for inhibiting the transmission of oxygen through a packaging type film. The rubbing resistance of the sulfuric acid catalyzed systems are also outstanding as shown by the data of the Table.

TO_2 AND RUBBING RESISTANCE OF PVOH COATING

(H_2SO_4 vs HN_4Cl)

Sample Code	Catalyst (phr)	P 613* Xlink (phr)	Rubbing Resistance 0WK	1WK	3WK	TO_2 (cc/100in^2) at 75% RH 1WK	3WK	App. 50% RH
C2388L	NH_4CL: 2.0	15	100	70	50	7.07	___	
C2389L	NH_4CL: 2.0	15	100	70	50	9.94	___	
Virton P	NH_4CL: 2.5	20	70	70	70	8.63	___	8.5 - 50.0
180-01P	H_2SO_4: 2.0	15	50	30	0	4.19	3.53	
220-01P	H_2SO_4: 2.0	25	50	50	0	4.69	3.86	
L9-05P	H_2SO_4: 2.0	20	50	30	0	3.14	3.24	
L9-10P	Nil	Nil	100	100	100	4.64	7.03	
L9-11P	H_2SO_4: 3.0	20	10	0	0	1.69	2.78	

* Parez 613, a methylated melamine formaldehyde

The cross-linked poly(vinyl alcohol) coated films described above are intended to be adhesively laminated to either oriented or unoriented commercially available

thermoplastic films such as homopolymer polypropylene film, polypropylene with coated layers, polypropylene with slip additives, polypropylene with coextruded layers, opaque polypropylene, polyethylene, Nylon, polyethylene terephthalate, polycarbonate, polystyrene, etc. A particularly preferred class of films are the polyolefins.

CLAIMS

1. A film combination comprising a polymeric substrate susceptible of transmitting oxygen, at least one side thereof having been treated to a surface free energy of at least 35 dynes/cm; at least one treated side having a primer coating thereon; and on the primer coating, an oxygen transmission inhibiting layer comprising a poly(vinyl alcohol) and a cross-linking agent catalyzed with sulfuric acid.

2. A combination according to claim 1 wherein the substrate comprises an oriented homopolymer or copolymer of propylene.

3. A combination according to claim 2 wherein the poly(vinyl alcohol) is cross-linked with a methylated melamine formaldehyde, a trimethylol melamine urea formaldehyde, glyoxal and borax and catalyzed with sulfuric acid.

4. A combination according to any preceding claim wherein both sides of the substrate have cross-linked poly(vinyl alcohol) thereon.

5. A combination according to any preceding claim wherein one side of the substrate has a heat seal layer thereon.

6. A combination according to claim 5 wherein the heat seal layer comprises an acrylic polymer.

7. A combination according to any preceding claim wherein the primer comprises poly(ethyleneimine).

8. A combination according to any preceding claim wherein the substrate includes a coextruded comparatively thin propylene-ethylene copolymer layer on at least one side thereof.

9. A combination according to claim 8 wherein the substrate includes a coextruded comparatively thin propylene-ethylene copolymer layer on both sides thereof.

10. A combination of claim 8 or 9 wherein the propylene-ethylene copolymer is random and the ethylene is present in a minor proportion.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/11116

A. CLASSIFICATION OF SUBJECT MATTER
IPC(5) :B32B 7/12, 27/08
US CL :428/353, 354, 517, 518, 522
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 428/353, 354, 517, 518, 522

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,282,729 (RICHARDSON) 01 NOVEMBER 1966. See entire disclosure.	1-4
Y	US, A, 4,564,559 (WAGNER, JR) 14 JANUARY 1986. See column 3, line 52 through column 4, line 49.	1-4

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be part of particular relevance
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"O" document referring to an oral disclosure, use, exhibition or other means
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
22 FEBRUARY 1993

Date of mailing of the international search report
26 MAR 1993

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/11116

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5-10
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.